The Preparation and Properties of Cyanide and Thiocyanate Derivatives of Fluorocarbon Carboxylic Acids

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By

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INTRODUCTION

The study of the physical and chemical properties of fluorocarbon compounds is a new and rapidly expanding field of chemistry. As such, it seems appropriate to outline briefly the manner in which this field evolved.

Early History

From the time Moissan [24] first isolated and identified fluorine, it was discovered that its reaction with carbon produced a violent explosion. This reaction was, and still is, used as a demonstration of the high reactivity of fluorine; and, until 1926, was considered nothing more than a laboratory curosity. In that year Lebeau and Damiens [19] isolated and identified methforane from that reaction. In 1930, Ruff and Keim [30] isolated ethforane from the same reaction. In 1934, Swarts [37] identified ethforane as a product from the electrolysis of trifluoroacetic acid. Other investigators [31, 40] during this period identified ethforane as a product from a mixture of methforane and monofluorodichloromethane in the presence of an electric arc. Ethforene was also first isolated from this reaction.

The violent reaction between fluorine and carbon was finally tamed when Simons and Block [34] discovered that mercury or mercury salts catalyzed the reaction, eliminating its explosive character.

From their work the first series of fluorocarbons were prepared and identified; the properties of which were completely unanticipated. It was immediately evident that the foundation for a whole new field of chemistry had been established.

Because of certain desirable properties, the fluorocarbons were in demand during World War II; and, during the search for suitable means by which to prepare them, several processes were developed. The two major ones were the metallic fluoride process and the catalytic fluorination process. The former utilizes the reaction of a metallic fluoride, such as cobalt trifluoride, with an organic compound. The latter employs a metal catalyst such as silver or copper for the reaction of an organic compound with fluorine gas diluted with nitrogen. Also during this time, still another method was invented by Simons [36], the announcement of which appeared in 1949. This was the electrochemical process. By this method fluorocarbon compounds are prepared by passing an electric current through a hydrogen fluoride solution of an organic compound. This process is by far the most versatile method of obtaining fluorocarbon compounds.

Fundamental Aspects of Fluorocarbon Chemistry

The utilization of fluorocarbon compounds in fundamental research offers many opportunities in both theoretical and experimental chemistry. From the very beginning, investigations revealed the unusual physical properties of fluorocarbon liquids. Values for viscosity, surface tension, refractive index, verdet constants, the velocity of sound, and many other physical constants are very low as compared to those of organic liquids. Some of these physical constants are the lowest ever recorded for liquids. It is almost certain that further studies of these and other physical properties will greatly supplement our knowledge of the liquid state and other related problems in physics and chemistry.

The chemical properties of fluorocarbon compounds were as surprisingly different from those expected as were their physical properties. The chemical properties, of course, were assumed on the basis of analogy with organic chemicals. For example, fluorocarbon nitrides and oxides, which have respectively a carbon-nitrogen and carbon-oxygen skeletal arrangement equivalent to organic amines and ethers, are vastly different in chemical properties. Acetforamide does not undergo the Hofmann hypohalide rearrangement; rather, the two methforyl radicals couple to give ethforane.[7]

On the other hand, some fluorocarbon compounds undergo many reactions found in organic chemistry. For example, trifluoroacetic acid, which was perhaps the first fluorocarbon compound prepared [38], and other fluorocarbon carboxylic acids can be esterified with organic alcohols, the esters react with ammonia to give fluorocarbon amides, and the amides can be dehydrated with phosphorous pentoxide to yield fluorocarbon nitriles.

It is understandable then that without experimental evidence the empirical rules of organized organic chemistry are quite unreliable when applied to fluorocarbon compounds. This follows almost as a necessity when it is considered that the rules of organic chemical reactions are the result of the organization of a tremendous amount of experimental data; and further, that these data are essentially classified according to the properties of various functional groups. The fact that the properties of these functional groups are practically independent of the organic radical to which they are attached has obscured the distinction between the properties of a functional group and an organic compound containing that group. Only recently, by workers such as Hammett [8], have attempts been made to determine quantatively the influence of an organic radical on a functional group.

On the other hand, the effect of a fluorocarbon radical on a functional group is vastly different from that of an organic radical. This necessitates the accumulation of a great deal of experimental data, out of which will come the organized rules applicable to fluorocarbon compounds.

Up to now, experimental evidence indicates that there will be a certain amount of similarity in the chemical properties of both organic and fluorocarbon compounds. But for the most part, the chemical behavior of the latter is that of a separate and distinct order of chemical compounds. It will remain for future experimental results to determine the extent of the similarities and differences.

It is with this in mind that the present work is submitted, in the hope that the experimental results presented will contribute to the organization and understanding of the chemical properties of fluorocarbon compounds.

Fluorocarbon Carboxylic Acids

Until recently the only fluorocarbon carboxylic acid obtained in quantity was acetforic acid, prepared by the following series of reactions: [38]

$$C_6H_5CCl_3 \longrightarrow C_6H_5CF_3 \longrightarrow NO_2\text{-}C_6H_4\text{-}CF_3 \longrightarrow$$
$$NH_2\text{-}C_6H_4CF_3 \longrightarrow CF_3COOH\ .$$

The final step involves the oxidation of the meta amino compound by prolonged reflux with chromic acid. This method is long and tedious, but the yields are good for each step. This method was not used for the preparation of higher homologs because the alkforyl benzenes were not known.

Other methods by which the acids can be prepared are as follows:

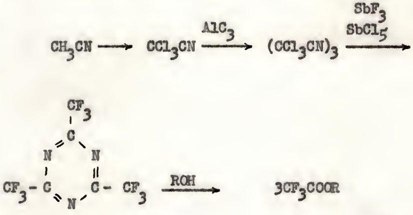
(a) [2] The hydrolysis of CF_3CCl_3 with concentrated sulfuric acid, catalyzed by mercuric sulfate, and the hydrolysis of compounds such as CF_3CH_2Br or CF_3CH_2Cl, preferably by potassium acetate, followed by oxidation of the alcohols.

(b) [10] The simultaneous oxidation and hydrolysis of olefins containing an alkforyl group,

$$3CF_3 - CCl = CCl_2 + 4KMNO_4 + 14KOH \longrightarrow$$
$$3CF_3CO_2K + 4MNO_2 + 3K_2CO_3 + 7H_2O + 9KCl\ .$$

By the use of symmetrical olefins such as CF_3-CCl=CCl-CF_3 [1], a less expensive product is obtained. This procedure can also be used for the preparation of dicarboxylic acids. Malonforic acid [12], for example, can be obtained from CH_2=CH-CF_2-CH=CH_2. Also, glutarforic acid [13] can be prepared from hexafluorodichlorocyclopentene in a similar manner.

(c) [28] The hydrolysis of a triazide. The steps for this method can be described as follows:



This method is currently employed as a limited industrial process.

However, the most promising general method of obtaining fluorocarbon carboxylic acids is by the electrochemical process. [36] At present, this method is the most satisfactory ones available for the commercial preparation of fluorocarbon carboxylic acids. Although their production is not on what could be considered a large scale, there is an increasing demand for these compounds, and this demand will eventually give rise to greater availability.

The physical and chemical properties of the fluorocarbon acids differ from their organic analogues in many respects. An excellent summary of some of their fundamental properties is presented in the book, "Fluorine Chemistry", [32] and in various technical bulletins [20] distributed by the Minnesota Mining and Manufacturing Company. In contrasting the behavior of fluorocarbon acids with that of organic acids, it is of particular interest to note such properties, low boiling points, very strong acidity, and the exceptional stability of the fluorine atoms to hydrolysis.

The carboxylic acid group in fluorocarbon acids has been found to form esters, acid halides, amides, anilides, anhydrides, aldehydes, etc. by conventional methods of preparation. However, there are many properties of the acid group that differ from the organic compounds. For example, the thermal decomposition of sodium acetforate gives the anhydride, acid fluoride, and products of complete decomposition rather than fluoroform. [38] Other sodium salts of this series undergo the following reaction:

$$R\text{-}CF_2\text{-}CF_2COONa \xrightarrow{heat} R\text{-}CF{=}CF_2 + CO_2 + NaF.$$

It is expected that further investigation of the properties of these compounds will reveal many other properties, the analogy of which will not be found in organic chemistry. This has been demonstrated by Crawford. [5]

Fluorocarbon Carboxylic Acid Chlorides

Fluorocarbon carboxylic acid chlorides can be prepared from the acid by all of the conventional methods of organic chemistry. Two methods of interest can be described by the following equations:

(1) [35] $(CF_3CO_2)Ba + PCl_3 \longrightarrow CF_3COCl$

(2) [11] $C_6H_5COCl + CF_3COOH \longrightarrow CF_3COCl + C_6H_5COOH$.

The first method gave yields of 53 per cent; the second, 79 per cent. However, Simons, Black, and Clark [33] report yields as high as 95 per cent by using phosphorous pentachloride with the pure acid.

The physical properties of the fluorocarbon acid chlorides differ from their organic analogues in the direction as was previously mentioned for other fluorocarbon compounds. Perhaps the most striking difference is in boiling points. Acetforyl chloride, for example, has a boiling point at -27°C.; acetyl chloride boils at 52°C. This difference can probably be attributed to the presence of hydrogen in the organic compound. However, no experiments have been reported with these compounds to support this.

Some of the chemical properties of the fluorocarbon acid chlorides can be expressed by the following equations:

(1) [20] $CF_3COCl + HI \longrightarrow CF_3COI + HCl$

(2) [14] $CF_3COCl + NaN_3 \longrightarrow CF_3CON_3 \longrightarrow CF_3NCO$

(3) [18] $CF_3COCl + (C_6H_5)_2Cd \longrightarrow CF_3COC_6H_5$

(4) [35] $CF_3COCl + C_6H_6 \xrightarrow{AlCl_3} CF_3COC_6H_5$

(5) [11, 39] $CF_3COCl + \xrightarrow{LiAlH_4} CF_3CH_2OH$.

It can be seen that their chemical behavior is in many cases similar to that of analogous organic compounds. But it must be mentioned that when comparing a particular reaction involving either a fluorocarbon or organic compound, many differences appear in the properties of the products.

Statement of the Problem

Because of the significant differences between the chemical behavior of fluorocarbon compounds and analogous organic compounds, it was desired to prepare some previously unreported fluorocarbon compounds and compare or contrast their physical and chemical behavior with organic compounds obtained by a similar reaction. For this, several rather obscure and controversial types of compounds were selected. It was hoped that the results obtained would contribute to the resolution of these controversies. The types of compounds investigated can be outlined as follows:

1. A study of some of the physical and chemical properties of the products obtained from the reaction of fluorocarbon carboxylic acid chlorides with silver cyanide and silver thiocyanate. Included are the infrared absorption data of these compounds and the absorption data of organic compounds obtained by an analogous reaction.

2. The preparation of mercury derivatives of fluorocarbon amides.

3. The preparation of α-hydroxyalkforylmalonamides. Included for these compounds are their sodium salts, mercury derivatives, and sodium salts of the mercury derivatives.

EXPERIMENTAL PROCEDURES

Fluorocarbon carboxylic acids—The fluorocarbon monocarboxylic acids used in these experiments were obtained from the Minnesota Mining and Manufacturing Company. They were purified by distillation from an equal volume of concentrated sulfuric acid and fractionated by a column of approximately fifty plates. The pure acids were collected in glass vials, sealed, and stored until used.

Glutarforic acid—This acid was prepared by the alkaline permanganate oxidation of hexafluorodichlorocyclopentene according to the procedure of Henne and Zimmerschield.[7] The pure acid was collected in glass vials and then sealed.

Fluorocarbon carboxylic acid chlorides—The acid chlorides were prepared by the addition of the fluorocarbon acid to 1.5 equivalent of phosphorous pentachloride. The first two members of the series were distilled from the reaction mixture, collected in a trap cooled by dry ice acetone, and transferred to either a reaction vessel or to a storage bulb. Further purification was found unnecessary. Other members of the series were fractionated directly from the reaction mixture by a column of approximately fifty plates.

Glutarforyl chloride—A rubber stopper was placed on the neck of a sealed glass vial containing 27 g. (0.11 mole) of glutarforic acid. The tip of the vial was broken and the stopper inserted into one neck of a 500 ml. three-neck flask, equipped with a stirrer and reflux condenser, and containing 52 g. (0.25 mole) of phosphorous pentachloride. By heating the vial with a small flame, the acid melted and slowly dropped into the reaction flask. After the addition of the acid, the mixture was refluxed with stirring for thirty minutes. The mixture was then fractionated. The yield of colorless liquid, b.p. 75-6°C., was 16.6 g. (0.06 mole).

Analysis—Since this compound hydrolyzes readily in water, the silver chloride gravimetric analysis was used on the aqueous solution.

Calculated for $C_5F_6O_2Cl_2$: Cl, 25.63%

Found: Cl, 25.56%

Fluorocarbon Carboxylic Acid Cyanide Dimers

All of these compounds were prepared by the same method. The only difference among the preparations was the reaction time, which ranged from three days for the first member to three weeks for the last member. The compounds are summarized in Table I.

The first member of the series will serve as an example of their preparation.

Trifluoroacetyl cyanide dimer—Approximately 0.05 mole of trifluoroacetyl chloride was transferred to a heavy-wall glass vial containing 10.7 g. (0.08 mole) of dry silver cyanide. The vial was sealed and placed in a water bath for three days with the temperature

TABLE I

Fluorocarbon Carboxylic Acid Cyanide Dimers

$(RCOCN)_2$ R	B.p., °C.	d_4^{25}	CN Analysis, %		M. Wt. of Vapor	
			Theory	Found	Theory	Found
CF_3-	83-4	1.440	21.14	20.92	246	245
CF_3CF_2-	106-08	1.532	15.03	14.77	346	346
$CF_3CF_2CF_2$-	136-38	1.606	11.66	11.52	446	444
$CF_3(CF_2)_4$-	190-93	1.719	8.05	7.63	646	-

maintained at 80-95°C. The vial was cooled in liquid air, opened and attached to a vacuum manifold system and the liquid contents transferred to another vial. The second vial was then removed from the manifold system and the contents transferred to a small fractionating apparatus, avoiding as much as possible contact with atmospheric moisture. The product was then fractionated. The yield of colorless, mobile liquid, b.p. 83-4°C., was 5.0 g. (0.04 mole).

Analysis--Since this compound hydrolyzes readily in water, advantage was taken of this by using the silver cyanide gravimetric analysis method on the hydrolyzed solution.

Vapor density--The molecular weight in the vapor was calculated by measurements of the vapor density. This was done by weighing a known volume of the gas at a known temperature and pressure. A bulb of measured volume carrying a stopcock and ground joint was attached to a vacuum system, exhausted, and filled with the vapor under investigation at a measured pressure and temperature. The bulb was then removed and weighed. The results are indicated in Table I. Table II shows the molecular weight of the methforyl compound at constant temperature with varying pressure.

Reaction with excess water--A small glass vial, sealed and containing 4.73 g. (0.02 mole) of trifluoroacetyl cyanide dimer was placed in a 125 ml. Erlenmeyer flask containing 25 ml. of cold distilled water, stoppered, and immersed in an ice bath. The vial was broken by the action of a magnetic stirrer, and the reaction was complete in about ten minutes. Hydrogen cyanide was removed

TABLE II

Molecular Weight of Trifluoroacetyl Cyanide Dimer

Temp., °C.	Vol., cc.	Weight, g.	Pressure, mm/Hg	Molecular Weight Theory	Molecular Weight Found
33	214	0.2092	77.0	246	245
33	214	0.1270	46.2	246	246
33	214	0.0762	27.5	246	246
33	214	0.0271	9.1	246	268

by fractionation. The remaining solution was titrated with standard sodium hydroxide using phenophthalein indicator. The results indicated two equivalents of trifluoroacetic acid for each equivalent of the acid cyanide compound.

On another sample, trifluoroacetic acid was identified after removing the hydrogen cyanide by extracting the solution with ether, removing the ether, and fractionating the residue from an equal volume of sulfuric acid.

Reaction with an equivalent amount of water---By the same method as employed above, 5.92 g. (0.02 mole) of trifluoroacetyl cyanide dimer was mixed with 0.35 ml. (0.02 mole) of cold distilled water. When the reaction was complete, the mixture was carefully fractionated. The only products obtained were hydrogen cyanide and trifluoroacetic anhydride.

Reaction with excess alcohol---The above procedure was employed for the reaction of trifluoroacetyl cyanide and n-butyl alcohol. The products obtained were hydrogen cyanide and n-butyl trifluoroacetate. They were identified by fractionation.

Reaction with an equivalent amount of alcohol---The above procedure was employed for the reaction of trifluoroacetyl cyanide dimer with an equivalent amount of n-butyl alcohol. Upon fractionation, only hydrogen cyanide, n-butyl trifluoroacetate, and trifluoroacetyl cyanide dimer were obtained.

Reaction with an equivalent amount of trifluoroacetic acid---The above procedure was employed for the reaction of trifluoroacetyl cyanide dimer with an equivalent amount of trifluoroacetic acid. The only products obtained were hydrogen cyanide, the acid anhydride, and the cyanide dimer.

Reaction with silver or mercuric fluoride—Trifluoroacetyl cyanide dimer was added to an excess of dry silver or mercuric fluoride. Only one volatile product was obtained. This was identified by molecular weight calculations from vapor density measurements as trifluoroacetyl fluoride.

α -hydroxyalkforylmalonamides

α-hydroxymethforylmalonamide—22g. (0.09 mole) of trifluoroacetyl cyanide dimer was added to 50 ml. of cold concentrated hydrochloric acid in a 250 ml. Erlenmeyer flask. The flask was stoppered, placed in an ice bath, and allowed to stand overnight. The white crystalline precipitate that formed was broken up with a glass rod and 50 ml. of cold water added. The mixture was cooled in an ice bath and then filtered. The white crystals were washed several times with water and dried. The yield of crude product was 7.3 g. (0.04 mole). Two recrystallizations from benzene afforded pure α -hydroxymethforylmalonamide in the form of white needles, m.p. 150-51°C.

$$CF_3C(OH)(CONH_2)_2$$

α -hydroxymethforylmalonamide

TABLE III

Molecular Weight of Acetyl Cyanide Monomer

				Molecular Weight	
Temp., °C.	Vol., cc.	Weight, g.	Pressure, mm/Hg	Theory	Found
29	214	0.0490	63	69	68
29	214	0.0291	37	69	69
29	214	0.0187	23	69	71
29	214	0.0117	14	69	73

After filtering the acid solution from the above, it was extracted with ether, the ether removed, and the residue fractionated from an equivalent volume of concentrated sulfuric acid. This gave 3.6 g. (0.03 mole) of trifluoroacetic acid.

The other members of the hydroxyalkforylmalonamide series were prepared by the same procedure. The compounds are summarized in Table IV.

Reaction with sodium ethoxide—A solution, formed by adding 0.1 g. of sodium to 10 ml. of 95% ethanol, was added to a solution of 1.0 gram of α -hydroxymethforylmalonamide in 10 ml. of 95% ethanol. A white precipitate formed immediately. This was washed several times with warm ethanol and dried. The salt was readily soluble in water and gave a strongly alkaline solution. Acidification of this solution returned the original α -hydroxymethforylmalonamide.

The sodium salts of the other malonamides were prepared by the same procedure. A summary of these compounds is presented in Table V.

Analysis—Sodium was determined by the Zinc Uranyl Acetate method.

Reaction with mercuric oxide—0.11 g. of α -hydroxymethforylmalonamide was dissolved in 10 ml. of 95% ethanol. About 0.2 g. of red mercuric oxide was added and the solution refluxed for 30 minutes. The hot solution was then filtered and the alcohol evaporated on a steam bath. The glass-like product was pulverized,

TABLE IV

α -hydroxyalkforylmalonamides

$RC(OH)(CONH_2)_2$ R	M.p., °C.	% Nitrogen Theory	% Nitrogen Found	% Fluorine Theory	% Fluorine Found	% Carbon Theory	% Carbon Found
CF_3-	150-51	15.05	15.22	30.64	30.12	25.81	25.77
CF_3CF_2-	124-25	11.86	11.61	40.25	39.96	25.42	25.32
$CF_3CF_2CF_2$-	159-60	9.79	9.16	46.50	46.41	25.17	25.05
$CF_3(CF_2)_4$-	170-71	7.25	7.03	54.14	53.44	24.87	24.42

TABLE V

Sodium Salts of α - hydroxyalkforylmalonamides

$R-C(O)(CONH_2)_2$ Na R	M.p., °C.	% Sodium		% Nitrogen	
		Theory	Found	Theory	Found
CF_3-	170-75 (dec.)	11.06	11.21	13.46	13.29
CF_3CF_2-	160-70 (dec.)	8.91	9.10	10.84	10.71
$CF_3CF_2CF_2-$	173-78 (dec.)	7.46	7.63	9.09	8.88

leached several times with hot water, and dried. The yield of pure product, m.p. 212-15°C. (dec.), was 0.14 g. The mercury compound was soluble in hot alcohol and ethyl ether; insoluble in water.

Analysis--The mercury analysis was performed according to the procedure of Rauscher.[19]

The mercury compounds of other α-hydroxyalkforylmalonamides were prepared by the same procedure. They are summarized in Table VI.

Reaction with aqueous sodium hydroxide--To 5 g. of α-hydroxymethforylmalonamide was added 30 ml. of 30% aqueous sodium hydroxide solution in an apparatus similar to that used for Kjeldahl nitrogen determination. The mixture was allowed to stand overnight with the tip of the receiving condenser immersed in 25 ml. of standard hydrochloric acid. The solution was then steam distilled until the total volume in the receiving flask was 150 ml. This was titrated with standard sodium hydroxide using methyl red indicator. The results indicated 1.86 equivalents of ammonia for each equivalent of α-hydroxmethforylmalonamide.

After steam distillation, the alkaline residue was acidified with 50% sulfuric acid. The carbon dioxide that evolved was passed through a calcium chloride drying tube and collected in a U-tube containing Ascarite. The weight of carbon dioxide corresponded to approximately one equivalent of the original amount of amide.

The acidic solution from above was extracted with three 20 ml. portions of ethyl ether and the ether removed. The colorless liquid that remained was very acid to pH paper and soluble in water. It was not identified further.

TABLE VI

Mercury Derivatives of α -hydroxyalkforylmalonamides

$\left[R\text{-}C(OH)(C_2O_2N_2H_3)\right]_2Hg$ R	M.p., °C.	% Mercury		% Nitrogen	
		Theory	Found	Theory	Found
CF_3-	212 (dec.)	35.09	34.82	9.82	9.71
CF_3CF_2-	246 (dec.)	29.85	29.79	8.36	8.28
$CF_3CF_2CF_2$-	282 (dec.)	25.97	25.67	7.27	7.16

Sodium salts of the mercury derivatives of α-hydroxyalkforylmalonamides--A solution of about 0.1 g. of the mercury derivative of α-hydroxymethforylmalonamide in 10 ml. of 95% hot ethanol was added to a hot solution made by adding about 0.1 g. of sodium to 10 ml. of 95% ethanol. A precipitate formed almost at once. This was filtered and the white precipitate washed several times with hot ethanol.

The sodium salts of the other mercury derivatives were prepared by this same method. The compounds are summarized in Table VII.

Analysis--Mercury was determined by the method mentioned previously. Sodium was calculated by dissolving the salt in water and titrating with standard hydrochloric acid using methyl red indicator.

Mercury Derivatives of Fluorocarbon Amides

Mercury trifluoroacetamide--About 0.1 g. of trifluoroacetamide and 0.2 g. of red mercuric oxide were placed in an 8-inch test tube. This was heated by an oil bath to 150-70°C. for five minutes. The mixture was then cooled, taken up in hot ethanol, and filtered. The ethanol was removed on a steam bath. The yield of pure, white, granular product was about 0.1 g., m.p. 222°C. (dec.).

Analysis--Mercury was determined by the method mentioned previously; nitrogen by Kjeldahl.

TABLE VII

Sodium Salts of the Mercury Derivatives of α -hydroxyalkforylmalonamides

$[RC(O)(C_2O_2N_2H_3)_2]_2Hg\ Na_2$ R	M.p., °C.	% Mercury		% Nitrogen	
		Theory	Found	Theory	Found
CF_3-	360	32.57	32.11	9.12	8.95
CF_3CF_2-	360	28.01	27.63	7.84	7.79
$CF_3CF_2CF_2$-	360	24.57	24.19	6.87	6.63

The mercury derivatives of other fluorocarbon amides were prepared by this same method. They are summarized in Table VIII.

Fluorocarbon Acid Thiocyanates

Trifluoroacetyl thiocyanate--Approximately 0.05 mole of trifluoroacetyl chloride was transferred to a heavy-wall pyrex glass vial containing 13.3 g. (0.08 mole) of dry silver thiocyanate. The vial was sealed and placed in a water bath for two days with the temperature maintained at 60-80°C. The vial was then cooled in liquid air, opened and attached to a vacuum manifold system, and the liquid contents transferred to another vial. The second vial was removed from the manifold system and the contents transferred to a small fractionating apparatus, avoiding as much as possible contact with atmospheric moisture. The product was then fractionated. The yield of colorless, mobile liquid, b.p. 72-4°C., was 4.8 g. (0.03 mole).

The other compounds of this series were prepared by the same procedure. They are summarized in Table IX.

Analysis--The analyses of these compounds were performed by the Parr bomb gravimetric analysis for sulfur. The molecular weights were calculated from vapor density measurements by the method described previously.

Reaction with water--About 4 ml. of trifluoroacetyl thiocyanate was added to 15 ml. of distilled water. A vigorous reaction took place. Upon cooling, the small amount of yellow precipitate

TABLE VIII

Mercury Derivatives of Fluorocarbon Amides

$(RCONH)_2Hg$ R	M.p., °C.	% Mercury		% Nitrogen	
		Theory	Found	Theory	Found
CF_3-	219	47.17	47.05	6.60	6.67
CF_3CF_2-	244	38.16	37.92	5.34	5.44
$CF_3CF_2CF_2$-	286	32.05	31.88	4.48	4.59

TABLE IX

Fluorocarbon Carboxylic Acid Thiocyanates

RCO(SCN) R	B.p., °C.	d_4^{25}	% Sulfur		M. Wt. of Vapor	
			Theory	Found	Theory	Found
CF_3-	72-4	1.369	20.64	20.82	155	154
CF_3CF_2-	87	1.503	15.61	15.84	205	205
$CF_3CF_2CF_2-$	106	1.644	12.55	13.13	255	256

that formed was filtered, washed several times with water, and dried. Sodium fusion of this substance gave a positive qualitative test for sulfur and nitrogen; negative for fluoride. It was assumed to be polymeric thiocyanic acid.

The filtrate from above gave a blood red color with the addition of ferric ion. The filtrate was extracted with three 5 ml. portions of ethyl ether, the ether removed, and the residue fractionated from an equivalent volume of concentrated sulfuric acid. Trifluoroacetic acid was the only product recovered.

Reaction with alcohol--The fluorocarbon acid thiocyanates reacted with ethanol and n-butyl alcohol to give the corresponding ester plus polymeric thiocyanic acid. The esters were identified by fractionation from the reaction mixture.

Acetyl Cyanide

Acetyl cyanide--This compound was prepared by the reaction of acetyl chloride and dry silver chloride according to the procedure of Hubner.[8]

Acetyl Cyanide Dimer

Acetyl cyanide dimer was prepared by allowing acetyl chloride and silver cyanide to react in a sealed glass vial for a period of two weeks with the temperature maintained at 85-90°C. The vial was cooled, opened, and the contents extracted with ethyl ether. The ether was removed and the residue fractionated. Pure acetyl cyanide dimer was obtained from the 210-14°C. fraction. The colorless liquid solidified when cooled and was recrystallized twice from 50% ethanol-water mixture. The yield of colorless plates, m.p. 69°C., was about 15%.

Acetyl Thiocyanate

Acetyl thiocyanate was prepared by the reaction of acetyl chloride and dry silver thiocyanate in a sealed tube. The procedure employed was identical to that used for the fluorocarbon analogue.

Infrared Spectra

The instrument utilized for the infrared absorption data was a Perkin-Elmer Model 21 double-beam infrared spectrophotometer.

For pure acetyl thiocyanate, a demountable cell consisting of two salt plates pressed together over the liquid was used. The cell was approximately 0.100 mm. thick. For acetyl cyanide dimer, a solution of the organic compound in carbon tetrachloride was used in the same cell. For all other compounds, a gas cell 5.0 cm. thick was used. The pressure of the vapor in the cell was slightly less than the vapor pressure of the specific compound used. The temperature was approximately 25°C. for all recordings.

In Table X three significant infrared absorption regions of the organic and fluorocarbon acid cyanide compounds are presented in tabular form. Band A is thought to be associated with an ester oxygen-carbon bond type.

TABLE X

Characteristic Infrared Absorption Regions of Fluorocarbon and Organic Acid Cyanides

Compound	Cyanide Absorption Wavelength (Microns)	Carbonyl Absorption Wavelength (Microns)	Band A Absorption Wavelength (Microns)
CH_3COCN	4.45-4.50 (m)	5.85-5.90 (s)	none
$(CH_3COCN)_2$	4.45-4.50 (m)	5.55-5.60 (s)	9.13-9.17 (s)
$(CF_3COCN)_2$	4.40-4.45 (m)	5.40-5.45 (s)	8.95-9.05 (s)
$(CF_3CF_2COCN)_2$	4.40-4.45 (m)	5.40-5.45 (s)	8.95-9.05 (s)
$(CF_3CF_2COCN)_2$	4.40-4.45 (m)	5.40-5.45 (s)	8.95-9.05 (s)

Note: (s)=strong (m)=medium (b)=broad

Table XI shows three characteristic infrared absorption regions of the fluorocarbon and organic acid thiocyanate compounds. Bands B and C are thought to be associated with the acid thiocyanate group of these compounds.

TABLE XI

Characteristic Infrared Absorption Regions of Fluorocarbon and Organic Acid Thiocyanates

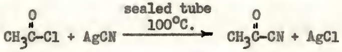
Compound	Band B Absorption Wavelength (Microns)	Carbonyl Absorption Wavelength (Microns)	Band C Absorption Wavelength (Microns)
CH_3COSCN	4.90-5.15 (s)(b)	5.70-5.80 (s)	6.55-6.60 (m)
CF_3COSCN	5.00-5.05 (s) 5.10-5.15 (s)	5.60-5.65 (s)	6.50-6.55 (m)
CF_3CF_2COSCN	5.00-5.15 (s)(b)	5.60-5.65 (s)	6.50-6.55 (m)
$CF_3CF_2CF_2COSCN$	5.00-5.15 (s)(b)	5.60-5.65 (s)	6.50-6.55 (m)

Note: (s)=strong (m)=medium (b)=broad

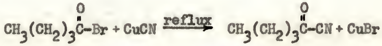
DISCUSSION

Organic Carboxylic Acid Cyanide Monomers

Organic carboxylic acid cyanide monomers have been known for many years, but have received very little experimental investigation. Actually, the investigations have been almost exclusively confined to methods of their preparation. This is partly understandable because a satisfactory method of preparation depends largely on the specific acid cyanide desired. The following equations represent satisfactory methods for the specific compounds indicated:

(a) [9] 

$$CH_3\overset{O}{\overset{\|}{C}}\text{-}Cl + AgCN \xrightarrow{\substack{\text{sealed tube}\\ 100^{\circ}\text{C.}}} CH_3\overset{O}{\overset{\|}{C}}\text{-}CN + AgCl$$

(b) [2] 

$$CH_3(CH_2)_3\overset{O}{\overset{\|}{C}}\text{-}Br + CuCN \xrightarrow{\text{reflux}} CH_3(CH_2)_3\overset{O}{\overset{\|}{C}}\text{-}CN + CuBr$$

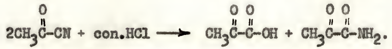
(c) [12]

$$CH_3O\text{-}C_6H_4\text{-}COCl + HCN \xrightarrow[\text{pyridine}]{\text{EtOEt}} CH_3O\text{-}C_6H_4\text{-}COCN + py\cdot HCl\ .$$

All of these reactions are accompanied by some degree of polymerization. The satisfactory methods are those least effected by polymerization.

The vapor of these compounds exists, for the most part, as a monomer. This is indicated in Table III for the first member of the series.

The reported chemical properties are few in number. They react with water and alcohols to yield respectively the parent acid or ester plus hydrogen cyanide, and they are hydrolyzed with concentrated hydrochloric acid according to the following equation:



$$2CH_3\overset{O}{\overset{\|}{C}}\text{-}CN + \text{con.}HCl \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + CH_3\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2.$$

Whitmore [27] has suggested a possible mechanism for this reaction. However, the mechanism lacks the support of experimental evidence.

Organic Carboxylic Acid Cyanide Dimers

Dimers of the aliphatic compounds have been obtained from the polymeric mixtures mentioned above. Other methods of preparation can be summarized in the following equations:

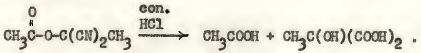
(a) [18] $4(CH_3CO)_2O + HCN \xrightarrow[190\text{-}200^{\circ}C.]{\text{sealed tube}}$

$(CH_3COCN)_2 + 2CH_3COOH$

(b) [9, 20] $2CH_3COCN \xrightarrow{Na} (CH_3COCN)_2$

(c) [10] $CH_2CO + HCN \xrightarrow{\text{heat}} (CH_3COCN)_2$

The structure of the dimer has been studied by Brunner [1] and is based on the products obtained by hydrolysis with concentrated hydrochloric acid. His results can be expressed in the following equation:



$$CH_3\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C(CN)_2CH_3 \xrightarrow{\substack{\text{con.}\\ HCl}} CH_3COOH + CH_3C(OH)(COOH)_2 .$$

Fluorocarbon Carboxylic Acid Cyanide Dimers

Attempts were made to prepare fluorocarbon acid cyanide compounds by a variety of methods. These included:

(a) The reaction of a fluorocarbon carboxylic acid chloride and silver cyanide in a sealed tube,

(b) The reaction of a fluorocarbon acid chloride, bromide, or iodide with cuprous cyanide in a sealed tube or under reflux,

(c) The reaction of a fluorocarbon acid chloride or bromide with hydrogen cyanide in an ether solution, using pyridine as a catalyst,

(d) The reaction of a fluorocarbon acid anhydride with hydrogen cyanide in a sealed tube or under reflux,

(e) By passing a fluorocarbon acid chloride through a hot tube containing silver, cuprous, cupric, mercuric, sodium, or potassium cyanide at pressures below atmospheric.

Method (a) was the only one from which a product other than starting materials was recovered.

Vapor density measurements indicate that these compounds exist as dimers of the simple formula. That there is no equilibrium with a monomer is indicated in Table II.

The chemical properties investigated can be summarized by the following equations:

1. $(CF_3COCN)_2 + 2HOH \longrightarrow 2CF_3COOH + 2HCN$

2. $(CF_3COCN)_2 + 2BuOH \longrightarrow 2CF_3COOBu + 2HCN$

3. $(CF_3COCN)_2 + HOH \longrightarrow (CF_3CO)_2O + 2HCN$

4. $(CF_3COCN)_2 + BuOH \longrightarrow CF_3COOBu + 1/2(CF_3COCN)_2 + HCN$

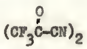
5. $(CF_3COCN)_2 + CF_3COOH \longrightarrow (CF_3CO)_2O + 1/2(CF_3COCN)_2 + HCN$

6. $(CF_3COCN)_2 + AgF \longrightarrow 2CF_3COF + AgCN$

7. $(CF_3COCN)_2 + HgF_2 \longrightarrow 2CF_3COF + Hg(CN)_2$

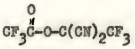
8. $(CF_3COCN)_2 + con.HCl \longrightarrow CF_3COOH + CF_3C(OH)(CONH_2)_2$.

The first five equations are consistent with either of the following two structures:



$(CF_3\overset{O}{C}\text{-}CN)_2$

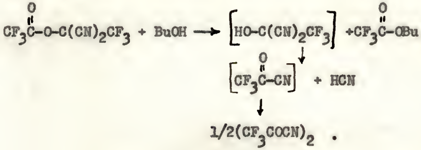
I



$CF_3\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C(CN)_2CF_3$.

II

For structure I, the reactions could represent simple replacements. Structure II requires hypothetical intermediates not uncommon to mechanistic pictures. For example;



$$CF_3\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C(CN)_2CF_3 + BuOH \longrightarrow \left[HO\text{-}C(CN)_2CF_3\right] + CF_3\overset{O}{\overset{\|}{C}}\text{-}OBu$$

$$\downarrow$$

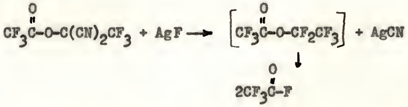
$$\left[CF_3\overset{O}{\overset{\|}{C}}\text{-}CN\right] + HCN$$

$$\downarrow$$

$$1/2(CF_3COCN)_2 \ .$$

The trifluoroacetyl cyanide monomer was not detected in any reactions from which it would be expected. This suggests that if formed, it undergoes a rapid dimerization.

Reactions 6 and 7 are also consistent with both structures I and II. However, in using structure II an unstable intermediate has to be assumed:



$$CF_3\overset{\overset{O}{\|}}{C}-O-C(CN)_2CF_3 + AgF \longrightarrow \left[CF_3\overset{\overset{O}{\|}}{C}-O-CF_2CF_3\right] + AgCN$$

$$\downarrow$$

$$2CF_3\overset{\overset{O}{\|}}{C}-F$$

That this intermediate would be unstable is in agreement with the fact that no hydrogen free fluorocarbon ester has ever been reported.

Reaction 8 decidedly favors structure II if it is assumed that the cyanide groups are hydrolyzed directly to amide groups without a carbon-carbon bond rupture; and further, that the ester link is broken in the usual manner. However, it should be kept in mind that these reactions, as with other chemical reactions, do not necessarily constitute a proof of structure.

α -hydroxyalkforylmalonamides

A significant difference between the organic and fluorocarbon acid cyanide dimers is shown by hydrolysis with concentrated hydrochloric acid.

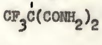
$$(CH_3COCN)_2 + \text{con.HCl} \longrightarrow CH_3COOH + CH_3C(OH)(COOH)_2$$

$$(CF_3COCN)_2 + \text{con.HCl} \longrightarrow CF_3COOH + CF_3C(OH)(CONH_2)_2$$

This can be explained only partially by the fact that fluorocarbon amides are slightly acidic and aliphatic organic amides are either neutral or slightly basic. The implication being that fluorocarbon amides are less susceptible to acid hydrolysis.

It was found that α -hydroxyalkforylmalonamides gave two equivalents of ammonia when treated with strong aqueous sodium hydroxide. Acidification of the basic solution gave one equivalent of carbon dioxide. From an ether extraction of the acidic solution, a colorless liquid was obtained. This liquid did not contain nitrogen, was soluble in water, and acid to pH paper. Further attempts to purify and identify this liquid were unsuccessful. It is presumed to be some form of an α -hydroxy acid, corresponding to the expected product of a typical malonic acid decarboxylation.

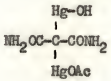
The α -hydroxyalkforylmalonamides react readily with sodium ethoxide to form a sodium salt. It is suggested that the sodium ion is associated with the oxygen of the hydroxyl group rather than with either of the amide groups. This is based partly on the fact that attempts to prepare a sodium salt of other fluorocarbon amides by this method were unsuccessful, and also on the behavior of the mercury derivatives. The simple ionic structure can be represented as follows:



$$CF_3\overset{O^-Na^+}{\overset{|}{C}}(CONH_2)_2$$

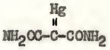
The α -hydroxyalkforylmalonamides react with mercuric oxide to form a mercury derivative. The analysis of both nitrogen and mercury indicates a ratio of two molecules of the diamide to each atom of mercury. This is not characteristic of the mercury derivatives of other diamides. For example, Menschulkin [13] has reported that succinamide has a ratio of one amide molecule to one mercury atom.

Naik and Patel [16, 17] prepared two different mercury derivatives of malonamide. They reported the following structures:



$$NH_2OC-\underset{\underset{HgOAc}{|}}{\overset{\overset{Hg-OH}{|}}{C}}-CONH_2$$

I



$$NH_2OC-\overset{\overset{Hg}{\|}}{C}-CONH_2$$

II

I was prepared by the action of mercuric acetate; II, by mercuric chloride. Although their studies were primarily concerned with the utilization of an active methylene group for carbon-mercury bond formation, it is of considerable interest that they reported no detection of a nitrogen-mercury bond. Since an active methylene group is quite impossible in fluorocarbon compounds, this helps to explain the difference of the ratio of diamide molecules to mercury in organic and fluorocarbon compounds.

All of these mercury derivatives were prepared by refluxing an ethanol solution of the amide with red mercuric oxide for about

30 minutes. It is of interest to report that if the reaction time was reduced to three or four minutes, a small amount of a water soluble mercury compound was isolated which had a ratio of one diamide molecule to one atom of mercury. This is presumably an intermediate mercuri hydroxide compound. It was not investigated further.

By refluxing the mercury derivatives with aqueous potassium iodide, mercuric iodide and the original amide were recovered.

That the hydroxyl groups of the mercury derivatives are available for chemical reaction is indicated by the formation of a disodium salt of the mercury derivatives. The ratio of sodium to mercury is two to one. The salt is soluble in water and forms a strongly basic solution. Acidification of this solution precipitates the original mercury derivative.

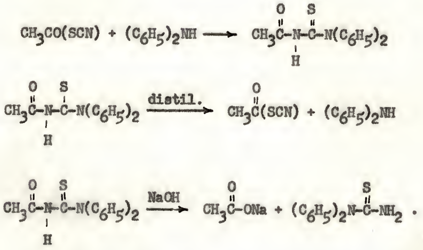
Organic Carboxylic Acid "Thiocyanates"

The term "thiocyanate", as applied to these compounds is used in a generic or descriptive sense, consistent with the mode of preparation. Complete evidence is lacking to distinguish between a true thiocyanate or isothiocyanate structure.

Organic carboxylic acid thiocyanates are obtained by the reaction of an acid chloride with lead thiocyanate. This reaction was first reported by Miquel.[14] Subsequent studies gave a rather good picture of their chemical properties. However, for the most part, these studies were stimulated by the concern of proving the exact structure of the acid thiocyanate group.

Hawthorn [6] first questioned the thiocyanate structure on the basis of Molar refraction. He assigned an empirical value to the thiocyanate and isothiocyanate groups and then calculated the Molar refractions of several acid "thiocyanates". His results suggested strongly an isothiocyanate structure. However, he could not resolve this with the fact that upon hydrolysis with water or alcohol, the compounds gave the parent acid or ester plus thiocyanic acid.

Dixon and Taylor [3] investigated the reaction of these compounds with diphenylamine and aniline with diphenylamine, the results indicated an isothiocyanate structure. This can be shown in the following equations:



$$CH_3CO(SCN) + (C_6H_5)_2NH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-N(C_6H_5)_2$$

$$CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\overset{S}{\overset{|}{C}}-N(C_6H_5)_2 \xrightarrow{\text{distil.}} CH_3\overset{O}{\overset{\|}{C}}(SCN) + (C_6H_5)_2NH$$

$$CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-N(C_6H_5)_2 \xrightarrow{NaOH} CH_3\overset{O}{\overset{\|}{C}}-ONa + (C_6H_5)_2N-\overset{S}{\overset{\|}{C}}-NH_2\ .$$

However, they found that the reaction with aniline, in boiling Xylene, gave 2.5% aniline thiocyanate and good yields of N-acetyl-N'-phenylthiocarbamide; but, at -10°C. gave 95% aniline thiocyanate and only traces of the thiocarbamide. Intermediate temperatures gave approximately equivalent amounts of these products. The conclusion would be, then, that these compounds are neither true thiodyanates or isothiocyanates. Their chemical behavior is not determined by any inherent feature of their structure, but dependent on external forces.

Fluorocarbon Carboxylic Acid "Thiocyanates"

Fluorocarbon carboxylic acid chlorides react with dry silver thiocyanate in a sealed tube to give excellent yields of the fluorocarbon acid "thiocyanate" compounds. Only poor yields were obtained when using lead thiocyanate in either a sealed tube or under reflux in a benzene solution.

The compounds are more stable than their organic analogues. This is based on the observation that freshly prepared samples showed very little signs of decomposition after several weeks in a sealed glass vial. The organic compounds, on the other hand, showed signs of decomposition after only a few days.

The molecular weights of both the fluorocarbon and organic compounds, calculated from vapor density measurements, indicates that the vapor is monomeric. Chemically, they react vigorously with water and alcohols to yield respectively the parent acid or ester plus thiocyanic acid.

Infrared Absorption

The infrared absorption data of the organic and fluorocarbon cyanide compounds offer a qualatative clue as to their structure.

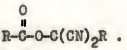
The organic monomer and dimer have two readily identifiable absorption regions in common. These are the carbon-nitrogen triple bond of the cyanide group and the carbonyl group. The former occurs at about 4.5 microns; the latter, at about 5.6 microns. In addition, the organic dimer has a moderately strong absorption peak at about 9.15 microns. That this was not due to being in the carbon tetrachloride solution was verified when the same band appeared in a Nujol Mull of this compound. It is quite probable that this peak is associated with an ester oxygen bond. It is in the region associated with such bonds. However, no information was found in the literature concerning an ester type comparable with the suggested structure of the organic dimer. The fluorocarbon dimers also have an absorption in this vicinity, occurring at about 9.00 microns for the first member of the series. They also have a carbon-nitrogen triple bond absorption at 4.4 microns and a carbonyl absorption at 5.45 microns. It is of interest to note that the shift to a shorter wavelength for each of these bands of the fluorocarbon compounds is of the same order of magnitude.

The fluorocarbon and organic acid "thiocyanates" have three significant absorption regions in common. For the organic compound, they appear at about 5, 5.75, and 6.60 microns. The fluorocarbon compounds have these bands at about 5.1, 5.6, and 6.5 microns. The second band of each is undoubtedly that due to the carbonyl group. However, the very strong absorption in the vicinity of 5 microns is quite an unusual location. Although the spectra of many sulfur compounds have been reported, a search of the literature revealed no compounds, thiocyanate, or isothiocyanate for which an infrared absorption had been reported for the 5.0 micron region; or for that matter, any other compound containing sulfur. It was thus necessary to prepare and determine the absorption spectra of acetyl thiocyanate for comparative purposes. However, one thing is clear: Whatever may be the exact structure of the acid "thiocyanate" group, the infrared spectra strongly suggests that the structures of the fluorocarbon and organic compounds are the same.

SUMMARY

The preparation and some of the chemical and physical properties of twenty-four previously unreported fluorocarbon compounds is presented. These compounds represent eight distinct molecular species. They can be summarized as follows:

1. A series of fluorocarbon carboxylic acid cyanide dimers were prepared and some of their chemical and physical properties determined. These compounds are believed to have the following structure:



$$R-\overset{O}{\overset{\|}{C}}-O-C(CN)_2R \ .$$

The specific compounds prepared were for R equals: CF_3-, CF_3CF_2-, $CF_3CF_2CF_2-$, and $CF_3(CF_2)_4-$. On the basis of molecular weight, calculated from vapor density measurements at constant temperature and variable pressures, it was determined that the vapor dimer is not in equilibrium with a significant concentration of a monomer. Also, the monomer was not obtained by using a variety of preparative methods from which it might be expected. It is suggested that either the monomer of this species is not formed or that it rapidly dimerizes. This is in sharp contrast to the organic analogues, the monomer and dimer of which are both known and convertible one into the other. In addition, the reaction of glutarforyl chloride with silver cyanide gave only an unidentified solid mass.

On the basis of the chemical reactions investigated and the infrared absorption data evidence is presented in support of a structure for the dimer. This structure is given above. If this is the structure, the reaction with silver and mercuric fluoride is additional evidence to support the theory that a hydrogen free fluorocarbon ester is either unstable and rearranges spontaneously to two molecules of the fluorocarbon acid fluoride or that it cannot be formed.

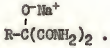
2. A series of α-hydroxyalkforylmalonamides were prepared and some of their physical and chemical properties determined. These compounds are believed to have the following structure:

$$R\text{-}C(OH)(CONH_2)_2 .$$

The specific compounds prepared were for R equals: CF_3-, CF_3CF_2-, $CF_3CF_2CF_2$-, and $CF_3(CF_2)_4$-. It was found that these compounds undergo a typical malonic acid decarboxylation when subjected to alkaline hydrolysis, followed by acidification. It was determined that the product was a strongly acidic fluorine containing compound. It is thought to be some form of an α-hydroxy fluorocarbon carboxylic acid.

3. A series of sodium salts of the α-hydroxyalkforylmalonamides were prepared. These compounds are believed to have

the following simple ionic structure:



$$\overset{O^-Na^+}{\overset{|}{\text{R-C}}}(CONH_2)_2 \text{ .}$$

The specific compounds prepared were for R equals: CF_3-, CF_3CF_2-, and $CF_3CF_2CF_2-$. Evidence is presented which indicates that the sodium ion is associated with the oxygen of the hydroxy group. A search of the available literature revealed that no salt of an analogous organic compound has been reported.

4. A series of mercury derivatives of α -hydroxyalkforylmalonamides were prepared. These compounds can be represented by the following formula:

$$\left[\text{R-C(OH)(CONH}_2\text{)(CONH)}\right]_2\text{Hg .}$$

The specific compounds prepared were for R equals: CF_3-, CF_3CF_2-, and $CF_3CF_2CF_2-$. The analytical data indicate that there are two molecules of the diamide to each atom of mercury. Evidence is presented which indicates that the mercury is associated with the amide group rather than the hydroxy group. The fact that two of the malonamide molecules are associated with one mercury atom is not in accord with the properties of organic diamides.[13, 16, 17] However, the arrangement of the association is not known.

5. A series of mercury derivatives of fluorocarbon amides were prepared. These compounds can be represented by a general

formula:

$$(RCONH)_2Hg.$$

The specific compounds prepared were for R equals: CF_3-, CF_3CF_2-, and $CF_3CF_2CF_2$-. The analytical data indicate that there are two molecules of the amide to each atom of mercury. This is similar to the properties of analogous organic amides.[13] However, in contrast to their organic analogues, the fluorocarbon mercury derivatives are insoluble in water.

6. A series of sodium salts of the mercury derivatives of the α-hydroxyalkforylmalonamides were prepared. These compounds can be represented by a general formula:

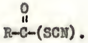
$$\left[RC(O)(CONH_2)(CONH)\right]_2HgNa_2 .$$

The specific compounds prepared were for R equals: CF_3-, CF_3CF_2-, and $CF_3CF_2CF_2$-. The analytical data indicate two sodium ions for each atom of mercury. This suggests that the sodium ions are associated with the oxygen of the hydroxyl groups. The salts are soluble in water, forming an alkaline solution. Acidification to a pH of about 6, precipitates the original mercury compound.

7. Glutarforyl chloride was prepared and identified by analysis.

8. A series of fluorocarbon acid "thiocyanates" were prepared and some of their physical and chemical properties determined. These compounds can be represented by the following structural

formula:



$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}(SCN).$$

The specific compounds prepared are for R equals: CF_3-, CF_3CF_2-, and $CF_3CF_2CF_2$-. Because of the striking similarity between the infrared spectra of these compounds and the organic acid "thiocyanates", it is concluded that the structures are the same. However, experimental evidence is inconclusive to distinguish between a true thiocyanate or isothiocyanate structure.

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BIOGRAPHICAL NOTE

Robert Hoover Patton was born on October 16, 1926, in Miami, Florida. In 1944 he entered college at the University of South Carolina, Columbia, South Carolina, in the Navy V-12 Program. While in this program he also attended Howard College, Birmingham, Alabama, and Georgia School of Technology, Atlanta, Georgia. Upon the curtailment of this program in 1946, he was honorably discharged from the Navy.

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COMMITTEE REPORT

This dissertation was prepared under the direction of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Science and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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